Glass and Ceramics, Vol. 67, Nos. 11 – 12, March, 2011 (Russian Original, Nos. 11 – 12, November – December, 2010)

ENAMELS

UDC 666.293

EFFECT OF P_2O_5 ADDITION ON Li_2TiO_3 CRYSTALLIZATION WITH OPACIFICATION OF WHITE SINGLE-LAYER GLASS ENAMEL COATINGS

E. A. Yatsenko[1]

Translated from *Steklo i Keramika*, No. 12, pp. 24 – 26, December, 2010.

The mutual effect of the components of enamel on its whiteness is examined. Effect of P_2O_5 on the process of opacification of white single-layer enamels is studied. It is established that Li_2TiO_3 plays the main role in the mechanism of crystallization.

Key words: single-layer glass enamel coatings, mechanism of opacification, crystallization, lithium titanate, phosphorus-containing microregion.

The most important problems of enameling household articles (gas stoves, refrigerators, water-heating columns, and others) are obtaining single-layer white and brightly colored coatings as well as lowering their firing temperature. Aside from lowering the cost of electricity, firing at lowered temperatures is advantageous because the firing decreases the degree of deformation of the metal and the number of defects caused by structural transformations in steel and absorption of hydrogen at high temperatures decreases [1].

For white, especially single-layer enamels, it is important to create conditions for and determine the mechanism of their stable predictable opacification [2]. Thus, the objective of the present work became the development of white, low-melting, single-layer enamels for dishware with lowered firing temperature and the following operational characteristics:

– the firing temperature must be no higher than 720°C;

– the enamels must not contain toxic and expensive components;

– the heat-treatment time of the enamels must be no longer than 7 min, special additional heat-treatment must be eliminated, i.e., the enamel must crystallize during natural cooling (with the furnace) after pouring.

The multicomponent system $R_2O – RO – B_2O_3 – Al_2O_3 – SiO_2 – TiO_2$ $(SnO_2, ZrO_2) – P_2O_5 – F$ taken as a base was modified in accordance with these requirements, specifically:

– fluorine-containing compounds were excluded from the mix because of their toxicity, even though they have a positive effect on the properties of glass (viscosity reduction during glassmaking, capability of opacifying glass, and so on);

– the B_2O_3 content was decreased because of toxicity and high cost;

– alkali-earth oxides were excluded from the glass and the SiO_2 content was reduced to increase fusibility;

– lithium, sodium, and potassium were used simultaneously, taking account of the polyalkali effect, as alkali oxides;

– since the coatings developed must be single-layered and must give a white color in a thin layer, TiO_2 was used as an effective opacifier.

To obtain glasses with the required properties [3] — establish regions of glass formation and set the character and degree of opacification — the following pseudoternary system was studied: $R_2O – TiO_2 – (B_2O_3 + SiO_2)$, where R = Li, Na, K.

A complex of studies showed that the main crystalline phase in all samples of optimal compositions is lithium titanate Li_2TiO_3 [3], which provides stable opacification. It was also established that the optimal alkali oxide ratio for opacification $Na_2O : K_2O : Li_2O$ is 1.0 : 0.4 : 0.5 wt.% or 1.0 : 0.4 : 1.0 mol.% [3]. Subsequent studies showed that the optimal compositions of opacified enamels contain small added amounts of Al_2O_3 and P_2O_5.

To determine the possibility of creating centers of crystallization by means of the oxides Al_2O_3 and P_2O_5 a series of experiments was carried out to establish the dependence of the degree of opacification on their content with a constant ratio of the concentrations of all other components. The

[1] South Russia State Technical University (Novocherkassk Polytechnical Institute), Novocherkassk, Russia (e-mail: yatsenko@mail.ru).

0361-7610/11/1112-0390

oxides Al_2O_3 and P_2O_5 in the amounts 2 wt.% (about 0.8 mol.%) were added as minor additives to the composition of the experimental glasses. It was found that Al_2O_3 content from 0.5 to 5.0%[2] and constant P_2O_5 content 2 wt.% has only a weak effect on the glass opacification intensity, since the values of the whiteness are in the range 80 – 85% and the brightness does not vary much and equals about 55%.

Thus, it can be supposed that P_2O_5 forms phosphorus-containing microregions, permitting the appearance of centers of crystallization where Li_2TiO_3 actively crystallizes. To confirm this mechanism of crystallization in a glass with the optimal composition the P_2O_5 content was varied from 0.5 to 5%, and the ratio of other components left unchanged. The composition of the synthesized glasses and their properties [4] are presented in Table 1.

As seen in Table 1, the degree of opacity (whiteness) increases with the P_2O_5 content to 2.5% (whiteness 85%) and then decreases somewhat, while the brightness decreases monotonically, but remains adequate to P_2O_5 content of 2.5% (whiteness 55%). For P_2O_5 content 5.0% the surface is matted. This is probably due to the appearance of weakly refracting sodium phosphate crystals, whose presence XPA established for these samples.

Thus, taking account of all indicators the optimal mass content of P_2O_5 corresponds to 2.0 – 2.5%. Since the requirement was to obtain a crystal glass material with high whiteness and brightness, density, and strength corresponding to the CLTE (about $120 \times 10^{-7}\ K^{-1}$), the crystallization had to be limited by P_2O_5 content 2.0 – 2.5%. Further crystallization of the glass is negligible, since the characteristics of the enamel obtained become degraded.

Figure 1 displays electron photomicrographs which were obtained by means of scanning electron microscopy of glass samples with P_2O_5 content — 0.5, 1.0, 2.0, 3.0, and 5.0%. Liquation structure is absent in all photographs. Likewise, liquation is not observed with prolonged (to 5 h) firings at temperatures 400, 500, and 600°C. The second phase with P_2O_5 content 0.5% is represented by isometric crystals about 1 μm in size and individual elongated crystals can be seen clearly. As the P_2O_5 concentration increases, the character of the crystals of the main phase remains unchanged, the number of crystals increases regularly with increasing P_2O_5 and for 5% P_2O_5 a second crystalline phase, belonging to sodium phosphate, becomes evident. XPA established that the main phase consists of lithium titanate Li_2TiO_3; in addition, weak reflections belonging to TiO_2 in the form of anatase as well as the phase Na_2SiO_3 are present in the diffraction pattern.

Thus, the optimal amount of P_2O_5 for obtaining good opacification is 2.0 – 2.5%, which corresponds to the P_2O_5 content chosen on the basis of the published data. There for the choice of the minimum P_2O_5 content, equal to 2.0%, is valid.

[2] Here and below, unless otherwise stipulated, the content by weight.

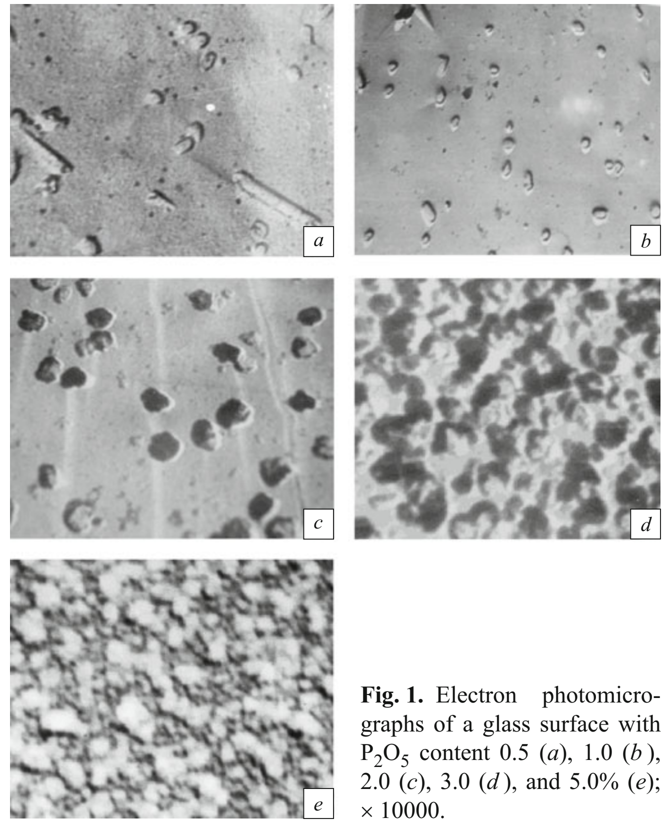

Fig. 1. Electron photomicrographs of a glass surface with P_2O_5 content 0.5 (*a*), 1.0 (*b*), 2.0 (*c*), 3.0 (*d*), and 5.0% (*e*); × 10000.

As indicated above, the main crystalline phase in the formation of coatings that gives high whiteness and other physicochemical properties is the phase Li_2TiO_3. It is known that the amount of the crystalline phase depends on the time the glass spends in the temperature interval of crystallization and therefore on the rates of heating and cooling. The thermal effects occurring with heating and cooling with rates 2, 15, and 50 – 80 K/min were studied in order to determine the main processes occurring with the formation of coatings.

Figure 2 shows thermograms obtained with heating and cooling of a sample of glass with the optimal composition for different rates of heating (Fig. 2*a*) and cooling (Fig. 2*b*). Three exoeffects were recorded with heating at 2 K/min; two of these effects are weak and occur at 500 and 550°C and probably are due to the crystallization of the phases TiO_2 and Na_2SiO_3; one is strong and occurs at 580°C and evidently belongs to the phase Li_2TiO_3, one endoeffect was recorded at 660°C and is due to the active crystallization of Li_2TiO_3. Weak endoeffects at 530 and 580°C are due to the crystallization of the phase Na_2SiO_3 and TiO_2, respectively. As the rates of heating and cooling increase, all these effects become weaker and shift to higher temperatures on heating and to lower temperatures on cooling. The heating and cooling regime with rates 50 – 80 K/min is as close as possible to conditions for depositing enamels, i.e., pouring and cooling without additional heat treatment.

To confirm that P_2O_5 forms centers of crystallization thermograms of glass with the optimal composition and no

TABLE 1. Compositions and Physicochemical Properties of Glasses

Composition	Content, wt.%								Brightness, %	Whiteness, %
	Na_2O	K_2O	Li_2O	SiO_2	B_2O_3	TiO_2	Al_2O_3	P_2O_5		
1	16.30	7.50	8.70	30.70	51.31	18.40	2.94	0	60	0
2	16.20	7.50	8.70	30.55	15.24	18.27	2.94	0.5	60	10
3	16.16	7.47	8.68	30.40	15.15	18.18	2.93	1.0	58	30
4	16.00	7.40	8.60	30.10	15.00	18.00	2.92	2.0	55	85
5	15.92	7.36	8.55	29.95	14.92	17.91	2.88	2.5	55	85
6	15.84	7.32	8.51	29.79	14.85	17.82	2.87	3.0	50	80
7	15.51	7.17	8.34	29.18	14.54	17.45	2.81	5.0	30	75

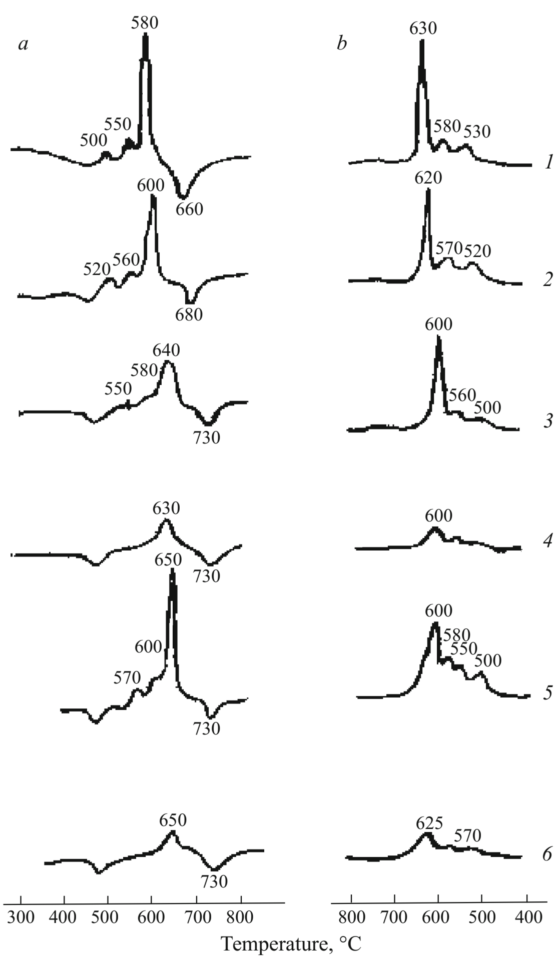

Fig. 2. DTA curves of glasses: *a*) heating; *b*) cooling, K/min; *1*, *2*, *3*) glass composition 4 (2% P_2O_5); *4*) composition 1 (no P_2O_5); *5*) composition 7 (5% P_2O_5); *6*) composition 2 (0.5 P_2O_5); heating and cooling rates 2 K/min (*1*); 15 K/min (*2*); 50 – 80 K/min (*3* – *6*).

P_2O_5 (see Fig. 2, curve *4*) and with 5% P_2O_5 (see Fig. 2, curve *5*) with rate 50 – 80 K/min were obtained. For both heating and cooling of glasses containing no P_2O_5 only weak crystallization of phases is observed, while the glass containing 5% P_2O_5 has intense peaks at 650°C (heating) and 620°C (cooling). In addition, a strong additional exoeffect is observed in the thermograms at 580°C. XPA showed the presence of sodium phosphate Na_3PO_4, which is also confirmed by the IR spectra of the sample of crystallized glass in which additional, marked, absorption bands are recorded at 1020 and 940 cm^{-1}, due to stretching vibrations of PO_4^{3-} groups (Fig. 3). The exoeffect due to the crystallization of Li_2TiO_3 is much weaker.

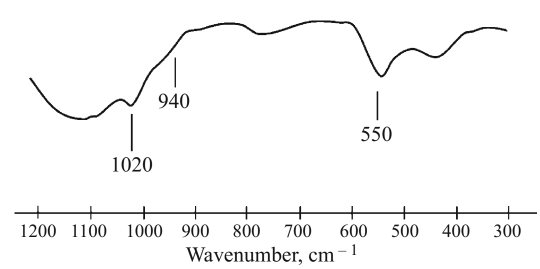

Fig. 3. IR spectrum of a sample of glass with composition 7 (5% P_2O_5) cooled at rate 50 – 80 K/min.

These investigations confirm that P_2O_5 plays the main role in the mechanism of crystallization of the glass.

In summary, additional heat-treatment, even with a high rate of cooling, is not necessary to obtain crystallized enamel with the experimental compositions if the required amount of P_2O_5 is present. The fact that the crystallization is rapid confirms the presence of ready phosphorous-containing centers of crystallization, on which Li_2TiO_3 crystallizes, in the melt.

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